

# PATENT SPECIFICATION (11)

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DRAWINGS ATTACHED



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## (54) METHOD AND APPARATUS FOR CONTROLLABLY MIXING REACTANTS

(71) We, THE GOODYEAR TIRE & RUBBER COMPANY, a corporation organized under the laws of the State of Ohio, United States of America, of 1144 East Market Street, Akron, Ohio, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to a method and to apparatus for controllably mixing liquid reactants having a short mixing time, with small reactant ratio deviation. The method and apparatus of this invention are particularly useful in the preparation of polyurethanes.

Various polymeric materials, particularly polyurethanes, are prepared by mixing liquid reactants with relatively short set-up times, e.g. 30 minutes or less. Thus, the hold-up time during mixing must normally be short and is often less than a minute. In a continuous-intermittent or continuous process of preparation of a polymeric material, it is typically necessary to control the ratio of reactants critically to within a 5 weight percent range of deviation, in order to achieve optimum properties of the product. If the ratio of these liquid reactants is not controlled within such narrow limits in a continuous-intermittent or in a continuous process, inferior products can be produced, which results in a considerable loss of material and equipment time as well as in a product having substantially inferior properties.

The present invention consists in a method which comprises continuously or continuously-intermittently charging at least two liquid reactants substantially in phase to a mixing chamber provided with mixing means to mix said reactants to form a reacting mixture and dispensing the reacting mixture from the mixing chamber, continuously sensing the pressure differential between the reactants charged into said mix-

ing chamber and, upon sensing a predetermined pressure differential, ceasing operation of said method.

The invention also provides apparatus for mixing liquid reactants, which comprises: a mixing chamber provided with mixing means to mix at least two liquid reactants to form a reacting mixture; at least two charging means to charge said liquid reactants continuously or continuously-intermittently and substantially in phase to said mixing chamber; a dispenser for dispensing said reacting mixture from said chamber; and sensing means to sense a pressure differential between said charging means and, upon sensing a predetermined pressure differential, to shut down said apparatus. It is of particular advantage that the mixing means in the mixing chamber should be a static blender, as compared with a rotary blender.

The invention is further illustrated with reference to the accompanying drawing, which shows a diagrammatic view of apparatus for controllably mixing fast reacting polyurethane reactants. The two reactants used to produce the final polyurethane in this apparatus are a polyurethane prepolymer or cement and a curative or chain extender in solution.

Reference to the drawing shows a liquid polyurethane prepolymer cement prepared from a polyisocyanate and a polyesterpolyol pumped from its storage tank 1 continuously-intermittently through a positive displacement pump 2 to the mixing chamber or head 3. Likewise, the curative in a solvent is pumped in phase with the prepolymer cement, from its storage tank 4 through a positive displacement pump 5 to the mixing chamber. Heat transfer jackets 6 and 7 are placed around each of the polyurethane prepolymer and the curative charging lines to maintain them at a temperature of about 25°C. The polyurethane prepolymer cement charge line and the curative charging line are operated at a pressure of about 1800 pounds per square inch gauge (psig) at the

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mixing chamber. The reactants are mixed in the mixing chamber or head by impinging upon and through a static blender composed of a resilient or rigid plastic gauze 8 having interstices therein and adapted to substantially fill the mixing chamber.

The polyurethane prepolymer and the curative charging lines are connected to a transducer 9 in a position less than about 30 internal diameters of the charging lines from the mixing chamber. The transducer is designed as a bi-directional differential type with an output varying depending upon the ratio of the applied pressures. The signal from the transducer is fed to a control 10 which actuates an alarm system 11 and a shutdown switch 12 when the differential pressure is greater than about 100 psig and preferably greater than about 50 psig for automatically shutting down the system when the differential pressure exceeds these limits.

The control 10 can also be used to actuate the solvent pump 13 to pump the solvent, such as methyl ethyl ketone, from its tank 14 to the mixing chamber to flush the reactants from the chamber. In a typical operation the solvent pump is normally manually actuated to clean the mixing chamber at the end of each continuous run and place it in condition for the next run.

In the description, the reactants are mixed with a static blender, rather than a rotary blender, which has been found to have particular utility because of the absence of moving parts. Various static blenders can be used, such as a mass of resilient or rigid plastic filamentary material loosely woven or stacked and having interstices therein. Representative of such plastic filamentary materials are those prepared from various resilient or rigid thermoplastic or thermoset polymers, such as polyethylene, polypropylene and polyesters, as well as other materials, such as glass and wire prepared from various metals such as steel and aluminium. It is generally desired that the blender does not tightly adhere to a polyurethane reaction mixture when cured.

Under the controlled conditions, the reactants are preferably controllably mixed in the mixing chamber having an average hold-up time of from about 1 to about 20 seconds and preferably from about 2 to about 10 seconds, and the reacting mixture dispensed through a dispensing line and sprayed onto a suitable substrate with a spray gun. The resulting coating on the substrate is then cured at a temperature of about 25°C. for about 8 hours to provide a cured polyurethane coating. If desired, the coating can be heated to provide shorter curing times such as about 4 hours at about 100°C.

In the practice of this invention, it is preferred that the reactants are charged into

the mixing chamber at a pressure of from about 1500 to about 3000 psig and at a temperature of from about 20°C. to about 50°C.

In the further practice of this invention, it is preferred that the pressure differential between the reactant charging lines at a position within about 100 and preferably within about 50 internal charge line diameters from the mixing head, be maintained within about 10 percent and preferably within about 5 percent. Thus, the sensing means is located at this position. In addition, particularly in the case of a continuous-intermittent charging of the reactants, it is preferred that the charge lines be operated substantially in phase, preferably within 5 percent, more preferably within 2 percent and most preferably about 4° of being in phase.

The polyurethane reaction mixtures used in the practice of this invention are typically prepared from reactive hydrogen-containing polymeric materials, an organic polyisocyanate and curatives selected from hydrocarbon diols and diamines having primary amino and primary and secondary amino groups. It is to be understood that the polyurethanes referred to in this specification may also contain polyurea linkages. Usually a solvent is added to the reaction mixture so that it will be in the form of a fluid mixture or solution. Generally, sufficient solvent is added to form a solution containing from 35 to 65 percent by weight of the mixture as solids. However, a higher or lower concentration of solids can be used, depending upon the reactants used and upon the intended use of the solution.

The reactive hydrogen-containing polymeric material used comprises at least one member selected from the group consisting of castor oil and materials having a molecular weight from 700 to 5000 and preferably from 1000 to 3000 selected from polyester polyols, polyesteramides, polyether polyols and hydroxyl terminated polymers of conjugated diene hydrocarbons having a hydroxyl functionality of from 2 to 3 and preferably from 2.1 to 2.5. Generally the polyester polyols and hydroxyl terminated diene hydrocarbon polymers are the preferred active hydrogen-containing material where high strength and solvent resistance are desired.

Representative examples of polyester polyols are the condensation products of low molecular weight polyols with an organic polycarboxylic acid or anhydride. Representative low molecular weight polyols are glycols such as ethylene glycol, propylene glycol, butylene glycol, pentylene glycol, decamethylene glycol, etc. Representative examples of the organic dicarboxylic acids that can be used are succinic acid, glutaric acid, adipic acid, 130

phthalic acid, terephthalic acid, isophthalic acid, suberic acid, sebacic acid, pimelic acid, and azelaic acid. The anhydrides of such acids can be used in place of the acid. If desired, from one to 20 percent by weight of a triol or higher polyfunctional polyol or polyfunctional acid can be present to produce branching in the polyurethane polymer.

Polyether polyols useful in preparing the polyurethanes used in this invention can be prepared by polymerizing or copolymerizing alkylene oxides such as ethylene oxide, propylene oxide, and butylene oxides, by polymerizing or copolymerizing the low molecular weight glycols, or by the reaction of one or more such alkylene oxides with the glycols or with triol, or with a polycarboxylic acid such as phthalic acid. The polyether polyols include polyalkylene-aryl ether glycols or triols, polytetramethylene ether glycols, polyalkylene ether-thioether glycols or triols, and alkyd resins. Generally, the polytetramethylene ether glycols are the preferred polyether glycols.

Representative examples of hydroxyl-terminated polymers of conjugated diene hydrocarbons are hydroxyl-terminated polymers of isoprene, of butadiene and their copolymers with minor amounts of vinyl compounds such as styrene and acrylonitrile.

Polyesteramides may be prepared by reacting a diamine, a glycol, and a dicarboxylic acid under conditions which will remove the water of condensation. Representative glycols and dicarboxylic acids useful in preparing polyesteramides are those useful in preparing polyesters, examples of which have already been shown. Various diamines may be used in forming the polyesters, examples of which are ethylene diamine, hexamethylene diamine, decamethylene diamine, cyclohexyl diamine, phenylene diamine, methylene dianiline, toluidine diamine, dichlorobenzidine and methylene-bis-chloroaniline.

The organic polyisocyanates used to prepare the polyurethanes include various organic diisocyanates and mixtures thereof. Generally the organic diisocyanates are preferred. The organic polyisocyanates can be aromatic, aliphatic or cycloaliphatic or combinations of these types.

Representative examples of such polyisocyanates include the toluene diisocyanates, m-phenylene diisocyanate, 4-chloro-1,3-phenylene diisocyanate, 4,4'-tetramethylene diisocyanate, 1,6-hexamethylene diisocyanate, 1,10-decamethylene diisocyanate, 1,4-cyclohexylene diisocyanate, 4,4'-methylene bis (cyclohexylisocyanate) and 1,5-tetrahydronaphthalene diisocyanate, and mixtures of such diisocyanates. For the purpose of the present invention, the toluene-diisocyanates, diphenylmethane-4,4'-diisocyanate and 3,3'-dimethyl-4,4'-bisphenylene diiso-

cyanate, are generally preferred although the diisocyanate having isocyanato groups connected to nonbenzenoid carbon atoms are preferred where color retention is important.

The polyurethane polymers are usually prepared by forming a liquid polyurethane reaction mixture by reacting a reactive hydrogen-containing polymeric material with a polyisocyanate to form an isocyanate terminated polyurethane which is then mixed with the diamine. The reaction mixture is then cured to form the polyurethane polymer. The isocyanate terminated polyurethanes can be prepared by reacting the reactive hydrogen-containing polymeric material with the organic polyisocyanate in proportions such that the ratio of isocyanate groups to the reactive hydrogen-containing groups of the reactive hydrogen-containing polymeric material is from 1.1/1 to 12/1 and preferably 1.2/1 to 2.5/1. These materials are generally reacted at temperatures from 20°C. to 150°C. The reactive hydrogens of the reactive hydrogen-containing polymeric material are supplied by hydroxyl groups and amino groups.

In the practice of this invention, the isocyanate-terminated polyurethane, sometimes called a prepolymer, is usually disposed or dissolved in a solvent to form a liquid cement. The diamine or hydrocarbon diol curative is then controllably mixed with the cement or prepolymer in a ratio of from 0.5/1 to 1.5/1 and preferably from 0.8/1 to 1.0/1 amino groups of the diamine or hydroxyl groups of the diol for each isocyanato group in excess of the reactive hydrogen groups of the reactive hydrogen-containing polymeric material. The cement is typically mixed with the curative at a temperature of from 20°C. to 50°C. and the mixture then typically cured at a temperature of from 20°C. to 150°C.

Representative of the various hydrocarbon diol curatives are ethylene glycol, 1,3-propanediol, 1,4-butane diol and glycerol.

Representative of various diamine curatives include aliphatic and aromatic diamines and particularly include compounds referred to in this specification as substituted methyl amine compounds.

Representative of the substituted methyl amine compounds are those having the formula  $R_1R_2R_3CNH_2$ , wherein  $R_1$ ,  $R_2$  and  $R_3$  are individually selected from the group consisting of (a) hydrogen radicals, alkyl, cycloalkyl, aryl, alkaryl, and aralkyl radicals. Representative of such radicals are alkyl radicals having from one to forty carbon atoms such as methyl, ethyl, propyl, isopropyl, butyl, isobutyl, amyl, isoamyl, hexyl, isohexyl, heptyl, octyl, duodecyl and tetracontyl radicals; cycloalkyl radicals such

as cyclobutane, cyclopentane, cyclohexane, cycloheptane and cyclooctane; aryl radicals such as phenyl and naphthyl radicals; alkaryl radicals such as tolyl and xylyl radicals, and aralkyl radicals such as benzyl radicals; and (b) substituted alkyl, cycloalkyl, aryl, alkaryl and aralkyl radicals where the substituents are selected from at least one of the group consisting of nitrogen, hydrogen, carbon, oxygen, sulfur, fluorine, chlorine, bromine, iodine and phosphorous. Representative examples of such substituted radicals are amino radicals, imino radicals, and radicals containing amino groups, imino groups, halo groups, ether groups and thioether groups.

Particularly representative substituted methyl amines are primary diamines having their amino groups attached to non-benzenoid carbon atoms.

Further representative examples of the said substituted methyl amine compounds are compounds prepared by the method which comprises reacting the substituted methyl amine compound of Formula (1) with an aldehyde or ketone. Various aldehydes can be used, representative of which are formaldehyde, acetaldehyde, propionaldehyde and benzaldehyde. Various ketones can be used representative of which are acetone, methyl ethyl ketone, methyl isobutyl ketone, diisobutyl ketone, methyl n-amyl ketone, methyl-i-amyl ketone and acetophenone. These compounds are generally called aldimines and ketimines.

Representative examples of the various diamines, including the substituted methyl amine compounds, are ethylene diamine, trimethylene diamine, tetramethylene diamine, hexamethylene diamine and dimethyl hexamethylene diamine; isophorone diamine, 1,4-cyclohexane bis methyl amine, 4,4'-diamino-dicyclohexyl methane, meta xylene diamine, paraxylene diamine, tetrachloro-paraxylene diamine, cyclobutane-1,2 bis methylamine, menthane diamine, imino bis propylamine, bis(amino propyl) piperazine, diethylene triamine, triethylene tetramine, triethylene pentamine, o- and m-phenylene diamine, o- and m-dichlorobenzidine, 2,5-dichlorophenylene diamine, 3,3'-dichloro-4,4'-diamino diphenyl methane, the naphthylene diamines, tolylene 2,4-diamine, p-amino benzyl aniline, and o- and p-amino diphenyl amine.

The non-reactive solvents normally used in making paints which are suitable for spraying are useful as solvents in this invention. Representative examples of these are benzene, toluene, the paraffinic naphthas, the naphthenic naphthas, the aromatic naphthas, ethyl formate, propyl formate, butyl formate, amyl formate, ethyl acetate, propyl acetate, methyl acetate, butyl acetate, amyl acetate, acetone, methyl ethyl ketone,

diethyl ketone, methyl isoamyl ketone, cellosolve acetate, cellosolve propylate, cellosolve acetate butyrate, dioxane, lower nitro-paraffins, etc. Mixtures of solvents may be used to obtain satisfactory spreading properties and evaporation rates when the polyurethane spray composition is applied to a polymeric surface.

If desired, pigments, surface-active agents, leveling agents, such as cellulose acetate butyrate, and other additives well known to the spray-coating art can be added to the solution or dispersion of the polyurethane reaction mixture. When a pigment is added, it is added in an amount from 0.5 to 10 parts and, preferably, in the amount from one to two parts of pigment per hundred parts of prepolymer by weight.

Submicroscopic pyrogenic silica has been found to be an effective thixotropic agent. This material is prepared by the vapor phase hydrolysis of silicon tetrachloride. Such silica, sold under the trademark CAB-O-SIL by Godfrey L. Cabot, Inc., is useful as a thixotropic agent in the sprayable polyurethane compositions when used in an amount of from 0.1 to 10 parts by weight per 100 parts of the prepolymer in the solution. The preferred amount is from 0.5 to 4 parts by weight. This range of pyrogenic silica gives improved thixotropic properties to the resulting sprayable composition.

The practice of this invention is further illustrated by reference to the following examples which are intended to be representative rather than restrictive of the scope of the invention. Unless otherwise indicated, all parts and percentages are by weight.

#### EXAMPLE I

An apparatus was constructed similar to that shown in Figure 1. In particular, a stainless-steel substantially cylindrical mixing chamber was provided having outside dimensions of about 6 inches height and 3 inches diameter with an internal capacity of about one pint. A resilient filamentous static blender was fitted inside the mixing chamber (obtained as Scotchbright from the 3M Company).

The apparatus further consisted of a positive displacement piston pump system for pumping the said polyurethane prepolymer cement and a curative solution to the mixing chamber. The system consisted of two cement pumps in parallel and one curative pump, the system being obtained as Model 205-208 Graco Hydrocat with a 4/1 mixing ratio from the Gray Company, Inc. "Graco" is a Registered Trade Mark. The polyurethane prepolymer cement and the curative solution were pumped to the mixing chamber through  $\frac{3}{8}$  inch stainless steel tubing. For cleaning convenience, a pump was connected to a methyl ethyl ketone solvent

storage container to pump solvent to the mixing chamber for cleaning upon shutdown.

A transducer was connected between the cement and curative  $\frac{3}{8}$  inch stainless steel feedlines at a position of about 12 inches directly before entering the mixing chamber. The transducer was a bi-directional differential type with an output varying depending upon the ratio of pressures between the polyurethane feedline and curative feedline. The transducer was obtained as Model PT-98D-10M from Dynisco, a Division of American Brake Shoe Company. The transducer was connected to a transducer translator, IB Instruments Model 110-3 with its output in turn connected to a controlling meter adjusted to actuate an audible alarm at a pressure differential of 100 psig.

The apparatus was operated on a continuous-intermittent basis by actuating the positive displacement cement and curative pumps to supply the cement and curative to the mixing head at a sufficient rate to provide a mixing holdup time within the chamber of 3 to 5 seconds. The system was operated at about room temperature or about 25°C. The pressure at the mixing chamber was adjusted to about 1800 psig and to within about 4 degrees of being in phase.

The mixture was dispersed from the mixing head through a spray gun and sprayed upon a substrate at about 25°C. to provide a coated article. It had a set-up time of about 20 minutes. The coating was cured for about 8 hours at about 25°C., although the curing rate could be accelerated by curing for about two hours at about 100°C.

By this method of operation, a commercially suitable coating was applied to the substrate. However, when the pressure differential between the cement line and curative line exceeded 100 psig, the resulting product had an excessively long setup time with inferior physical properties. Therefore, when a 100 psig pressure differential between the lines was detected automatically by the transducer with the corresponding audible alarm actuated, the system shutdown and the methyl ethyl ketone pump actuated to quickly clean the mixing chamber.

As hereinbefore disclosed, various polyurethane prepolymer cements and curative solutions can be used in the practice of this invention. For further illustrative purposes, a recipe, such as the following can be used: A prepolymer was prepared by reacting 6 moles of toluene diisocyanate with two moles of a polyester prepared by the condensation of adipic acid with an excess of a mixture consisting of 80 percent ethylene glycol and 20 percent propylene glycol and one mole of polyester prepared by the condensation of adipic acid with an excess of 1,4 butane

diol. This prepolymer was used to prepare a black master batch by mixing 240 parts of this prepolymer with 142 parts of carbon black, 86 parts of ethylene glycol monoethyl ether acetate and 377 parts of methyl ethyl ketone.

A mixture was then prepared by mixing 51 parts of a 10 percent solution of cellulose acetate butyrate, methyl ethyl ketone, 39 parts of submicroscopic silica (CAB-O-SIL) with a well dispersed mixture of 389 parts of ethylene glycol monoethyl ether acetate, 220 parts of methyl ethyl ketone and 82 parts of the prepared black master batch.

The polyurethane cement was then prepared by mixing 349 parts of this mixture with 548 parts of the said prepolymer.

The curative solution was made simply by mixing 199 parts of methylene dianiline with 538 parts of methyl ethyl ketone.

The prepolymer cement and curative solution are typically pumped to the mixing chamber so that from about 0.7 to about 0.9 moles of methylene dianiline are added for each mole of excess toluene diisocyanate over that equivalent to the polyester. Such a mixture typically remains operable by ordinary techniques at 25°C. for less than 10 minutes.

In the description of this invention, the term "set-up time" is used to describe the time between mixing the reactants and the time when the mixture has set-up to the extent that it is no longer sprayable by ordinary spraying techniques. Typically the reactants should be mixed in a substantially shorter time than the so-called "set-up time" in order to facilitate commercial production.

#### WHAT WE CLAIM IS:—

1. A method which comprises continuously or continuously-intermittently charging at least two liquid reactants substantially in phase to a mixing chamber provided with mixing means to mix said reactants to form a reacting mixture and dispensing the reacting mixture from the mixing chamber, continuously sensing the pressure differential between the reactants charged into said mixing chamber and, upon sensing a predetermined pressure differential, ceasing operation of said method.

2. A method according to claim 1, in which said reactants are continuously-intermittently charged to said mixing chamber by positive displacement pumps at a mixing chamber pressure of from 1,500 to 3,000 psig and within 5% of being in phase.

3. A method according to claim 1 or claim 2, in which said reactants are fed to said mixing chamber through charge lines, the pressure differential being sensed by means positioned within 100 charge line diameters from the mixing chamber, operation of said method being ceased upon sensing a

pressure differential greater than 100 psig.

4. A method according to any one of the preceding claims, in which said liquid reactants have a set-up time of less than 30 minutes and are (a) an isocyanate terminated polyurethane prepolymer and (b) a solution of a diamine or hydrocarbon diol curative for said polyurethane prepolymer.

5. A method according to claim 4, in which said isocyanate terminated polyurethane prepolymer is prepared from at least one organic polyisocyanate and at least one reactive hydrogen-containing polymeric material which is castor oil or a material having a molecular weight of from 700 to 5,000 selected from polyester polyols, polyester amides, polyether polyols and hydroxyl-terminated polymers of conjugated diene hydrocarbons having a hydroxyl functionality of from 2 to 3.

6. A method according to claim 3, in which said reactants are mixed in the mixing chamber with an average hold-up time of from 1 to 20 seconds, the sensing means being positioned within 50 charge line diameters of the mixing chamber and operation of said method being ceased upon sensing a pressure differential greater than 50 psig.

7. A method according to claim 1, substantially as hereinbefore described with reference to the accompanying drawings.

8. Apparatus for mixing liquid reactants and comprising: a mixing chamber pro-

vided with mixing means to mix at least two liquid reactants to form a reacting mixture; at least two charging means to charge said liquid reactants continuously or continuously-intermittently and substantially in phase to said mixing chamber; a dispenser for dispensing said reacting mixture from said chamber; and sensing means to sense a pressure differential between said charging means and, upon sensing a predetermined pressure differential, to shut down said apparatus.

9. Apparatus according to claim 8, in which said charging means comprise at least one positive displacement pump adapted to charge said reactants into said mixing chamber at a pressure of from 1,500 to 3,000 psig and within 5% of being in phase, the reactants being charged into said mixing chamber through charge lines and said sensing means being positioned within 100 internal charge line diameters from the mixing head and being adapted to shut down said apparatus when said pressure differential is greater than 100 psig.

10. Apparatus according to claim 8, substantially as hereinbefore described with reference to, and as shown in, the accompanying drawing.

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## COMPLETE SPECIFICATION

1 SHEET

This drawing is a reproduction of  
the Original on a reduced scale

